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This report will briefly outline some of the key findings made during the course of this project and some new work on the phase structure changes concomitant with the delamination behavior of Ta metallizations. Detailed accountants of prior work have been in included in previous "Interim Reports" of this Grant and in the many technical papers that have resulted from the support of this work. A complete list of these publications in provided in Appendix II of this Final Report.

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# FABRICATION OF HIGH-PERFORMANCE COATINGS SYSTEMS VIA A NOVEL IN-SITU/EX-SITU CHARACTERIZATION TECHNIQUE

FINAL REPORT:
JULY 31, 2001

by

John C. Bilello

U.S. ARMY RESEARCH OFFICE
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GRANT NUMBER: DAAG 55-98-1-0382

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# FABRICATION OF HIGH-PERFORMANCE COATINGS SYSTEMS VIA A NOVEL IN-SITU/EX-SITU CHARACTERIZATION TECHNIQUE

Final Grant Report: July 2002
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## Abstract

This report will briefly outline some of the key findings made during the course of this project and some new work on the phase structure changes concomitant with the delamination behavior of Ta metallizations. Detailed accountants of prior work have been in included in previous "Interim Reports" of this Grant and in the many technical papers that have resulted from the support of this work. A complete list of these publications in provided in Appendix II of this Final Report.

FINAL REPORT: July 31, 2002

By John C. Bilello

## Overview:

During the four years that this project has run a number of significant milestones have been reached. This Final Project report will not repeat the details of this work, which has been previously reported in previous "Interim Project Reports" and the numerous publications that are listed in the Appendix II of this paper. This report will concentrate on the highlights and include some new work done in the last eight months of the Grant, i.e. since the last Interim Report. Research focused on Ta refractory metal films.[1,2,3,4,5] The key development of this Grant was the construction, commissioning and ultimate utilization in thermo-mechanical testing of a novel *in situ* real-time synchrotron topography imaging facility. This equipment is has proven capable of examining the debonding limits of a number of refractory metal high temperature coatings. These observations have been coupled with real-time high resolution Bragg scattering studies to elucidate the concomitant phase and chemical structure of the film relating to the observed delamination modes. Finally, we will discuss some directions this work has pointed that would be worthy of future investigation.

## Experimental Methods:

A detailed report on the novel *in situ* real-time x-ray imaging stage and some experiments utilizing its capabilities has been given in previous references.[6,7] This stage has been upgraded to go to slightly higher temperatures (600C vs. 550C) and has been fitted with a temperature controller so that a variety of temperatures can be easily programmed into its test performance.[8] Figure 1 shows the capability of this control to be able to achieve a range of steady temperatures with variable ramp rates. This feature will allow future work that can accurately measure kinetic behavior by studies time dependent relaxation behavior as a function of temperature.

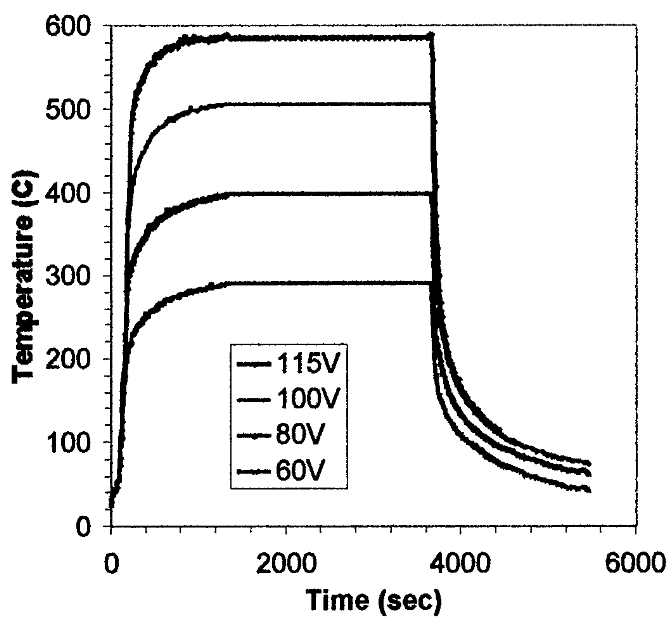


Figure 1

Variable temperature control of the in situ real-time synchrotron thermomechanical topography/radiography imaging stage.

We have also used our high resolution high energy 18kW Rigaku laboratory source, built under an earlier DARPA Grant, to observe

Bragg diffraction of thin Ta films as a function of time and temperature. By this means we were able to correlate the chemical phase structure of the films to their thermomechanical behavior.

Results and Discussion:

In may be recalled that in an earlier report it was shown that there was a critical working gas pressure that marked the region between adherent Ta films and those that rapidly debonded. Partial results were shown in the previous progress report (reference 2) and further work has been in the intervening period and is shown below in Table 1.

| Argon Pressure (mTorr) | Degree of Blistering | Spalling? |
|---|---|---|
| 2 | Major | Yes |
| 3 | Major | Yes |
| 5 | Major | Yes |
| 6 | Minor | No |
| 7 | Minor | No |
| 8 | None | No |
| 10 | None | No |
| 15 | None | No |
| 18 | None | No |

Table 1

Observed film delamination modes as a function of Ar working gas pressure during sputter deposition.

It is interesting (and significant) to note that no debonding was observed of any type when these films were subjected to high temperature testing in an oxygen environment. Why? Obviously, we wouldn't ask this question if we didn't have some inkling about what is happening. To clarify the behavior a series of Bragg scattering experiments were done as a function of time on a 600nm Ta film held at 600C at ambient.[9] The results are reported below in Figure 3.

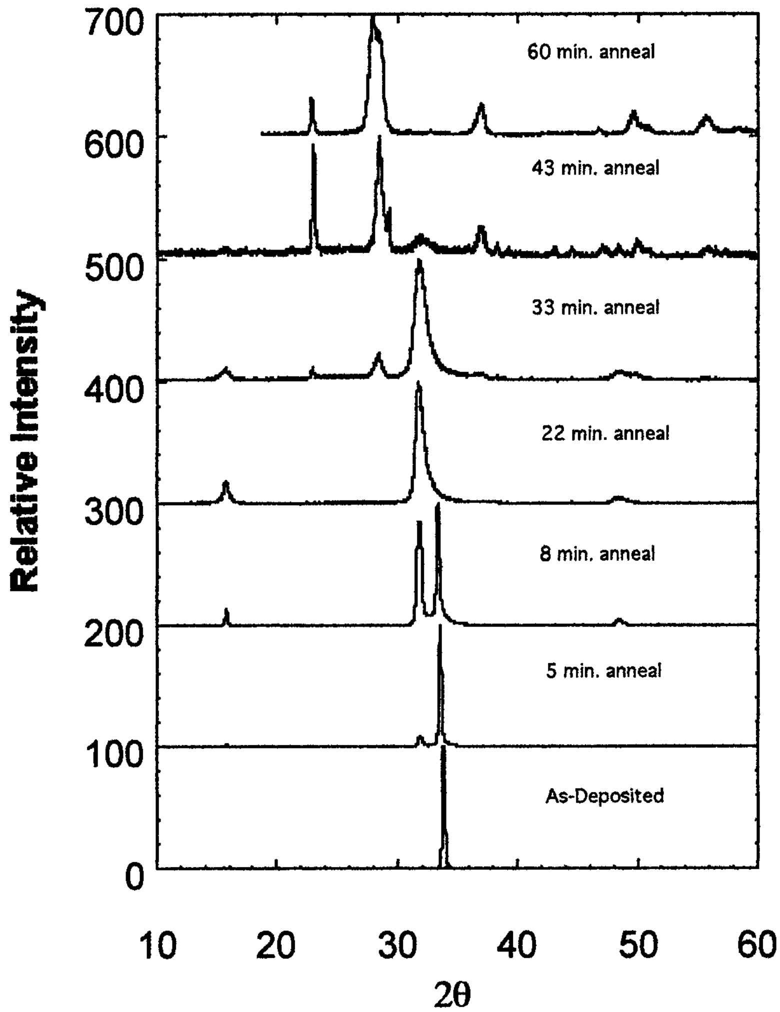


Figure 3 - Diffraction patterns at various times of a 600nm Ta film deposited at 2 mTorr Ar and annealed in ambient environment at 600C. Note the appearance of distinctive diffraction lines at various times - details explained in the text.

The initial "as deposited" diffraction plot shows a strong *out-of-plane* texture, hence the single intensive peak indicative of beta Tantalum. As the annealing procedures when 22 minutes is reached the film is seen to be converting to an unknown oxide (i.e. one not found in JCPDS files). Finally, by the 43 minute mark the film has converted to Tatalum pentoxide ($Ta_2O_5$). The next step was to correlate these findings directly with the morphology of these films as they are undergoing these phase transformations. This is displayed in Figure 4 below.

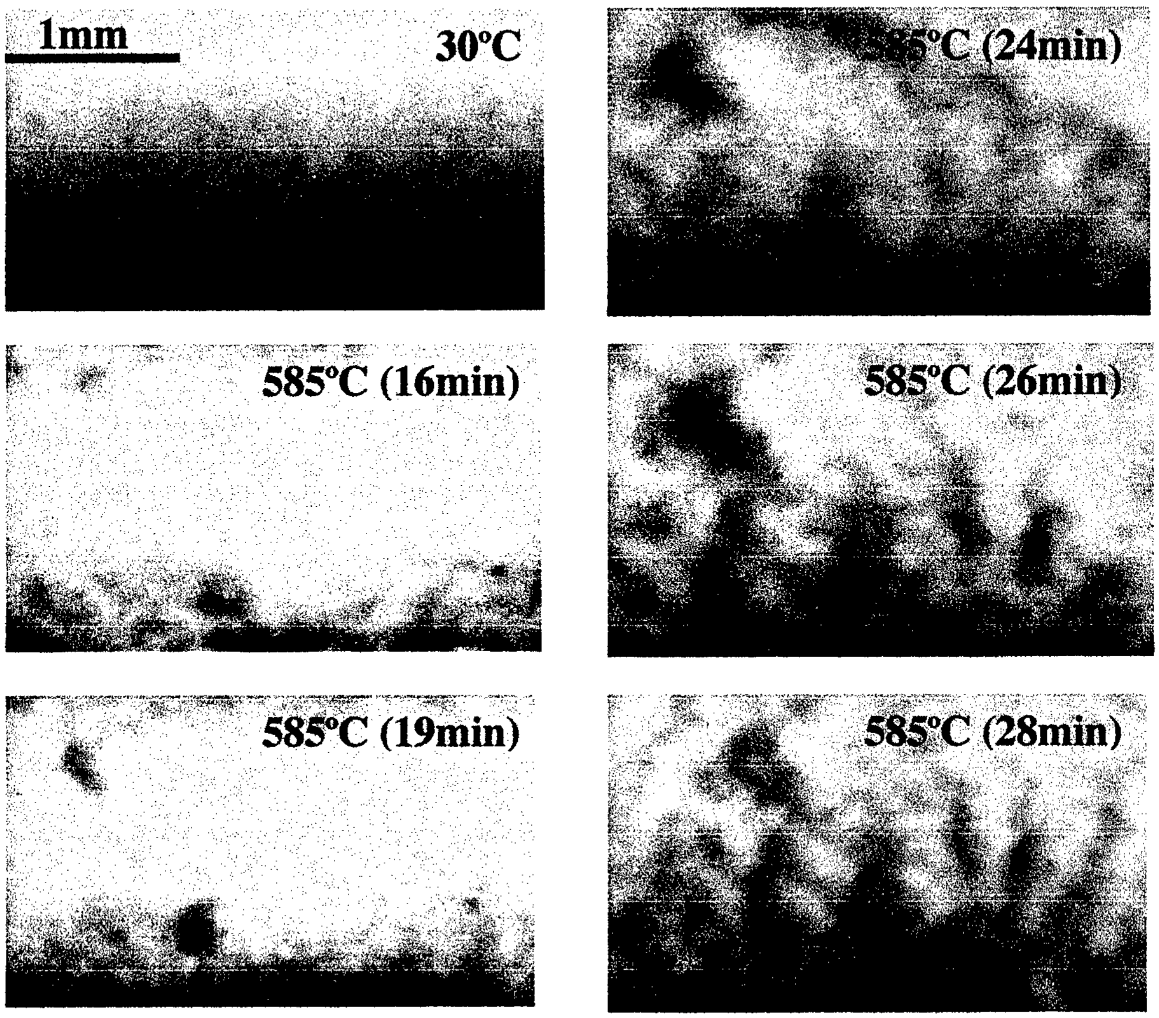


Figure 4 – Morphology of Ta films as a function of time annealed in ambient at 585C.

The small difference in temperature between the annealing run used for Bragg diffraction (Figure 3) and for the observed diffraction Topography/Radiography images is do to a slight mismatch in the calibration of the controllers on the two different instruments. Nevertheless the picture emerges that the film starts to blister, hence nucleating subsequent complete delamination effects, when the initial β-Ta deposition converts to an oxide. <u>But the story isn't this simple.</u> <u>Subsequent annealing/Bragg diffraction experiments on Ta films grown in the high pressure Ar regime that exhibited no delamination and excellent adhesion showed the same phase transformation sequence as a function of time.</u> This leads us to suspect that the real culprit here controlling delamination is the stress induced by the coefficient of thermal expansion (CTE) between the growing oxide phase in the transformation and the substrate. The films deposited at higher Ar working gas pressures are nominally less dense than those grown at lower pressures. This more open structure is probably able to accommodate the CTE mismatch strains and remain intact. If this is true it might provide a potent recipe for growing Ta (and perhaps other refractory films) in a manner that can enhance their thermo-mechanical stability. How to prove this supposition? What is needed is an in situ method of simultaneously measuring the strain (stress state) in the films as a function of time a temperature. Also parallel studies using Transmission Electron Microscopy (cross-section mode) to study the interfaces at adhesive and decohesive regions of the films are of interest. The ability of synchrotron diffraction topography/radiography to find critical regions is critical to these subsequent experimental plans. These areas will be explored as part of a new program sponsored by ARO in the future.

## Summary:

A novel new method for directly observing the thermo-mechanical response of refractory metal coatings has been developed. This technique relies on a thermo-mechanical stage capable of *in situ* real-time imaging of the mechanical behavior of film overlays on a high intensity synchrotron beam line. This facility has been able to take action sequence x-ray images at a rate of 30/sec at temperatures as high as 600C and record the film response to the thermo-mechanical conditions imposed.

The x-ray images of the morphology of the films as a function of time and temperature in an oxidizing environment (ambient) has been supplemented by time dependent Bragg diffraction studies of the chemical phase structure of the films. The results have shown that the $\beta$ -Ta films eventually converts to $Ta_2O_5$ upon annealing, which could induce a critical CTE mismatch leading to film failure if not properly accommodated by the film microstructure.

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[7] ARO Interim Progress Report, GRANT NUMBER: DAAG 55-98-1-0382, January 1, 2001 to December 31, 2002.

[8] B. L. French and J. C. Bilello, *Real-time In Situ Imaging of the "Delamination of Thin Ta Films on Si (100) Substrates via a Synchrotron Radiation Technique*, Eds. By C. S. Ozkan, L. B. Freund, R. C. Cammarata, and H. Gao, MRS Symp. Proc. 695, 385, (2002).

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# Appendix I

## Awards

John C. Bilello, Awarded a Senior NATO Visiting Fellowship to the Department of Materials, Oxford University, Oxford, United Kingdom, (2001). Renewed 2002-2004

John C. Bilello, Appointed Department Fellow, Department of Materials, Oxford University, Oxford, United Kingdom, (2001 and 2002).

# Appendix II

## PUBLICATIONS AND OF SCHOLARLY ACTIVITY: (Through Grant completion date - July 31, 2001)

### Publications in Refereed Journals and Books:

J. F. Whitacre, Z. U. Rek, S. M. Yalisove, and J.C. Bilello, *Phase Content and Stress State in Sputtered Nanoscale* Ta/$Ta_2O_5$ *Films,* to be submitted to Thin Solid Films (2002).

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Mechanical Properties IX, Accepted for Publication (2002) MRS Proceedings, in Press.

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M. J. Daniels and J. C. Bilello, *Characterization of Nanoscale Materials Structures via High Resolution Synchrotron Scattering, Nano-technology*, Eds. M. A. Fortes and P. J. Ferreira, IST Press, Lisbon, Portugal, (2001), Chapter in Book.

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J. F. Whitacre, J. C. Bilello and S. M. Yalisove, *In-Plane Texturing in Films and Coatings*, Textures and Microstructures, Textures and Micro-structures, TMS, Pittsburgh, PA, 34, 91 (2000).

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Z. B. Zhao, Z. U. Rek and J. C. Bilello, *Observation of the adhesion of thin Ta polycrystalline films to Si wafers via in situ topography/radiography*, Phil. Trans. Royal Soc. Lond. A, 357, (1999), p. 2681.

A. K. Malhotra, J. F. Whitacre, Z. B. Zhao, J. Hershberger, S. M. Yalisove and J. C. Bilello, *An In-situ/Ex-situ X-ray Analysis Stystem for Thin Sputtered Films*, Surface and Coating Tech., 110, (1998), 105-110.

J. F. Whitacre, Z. U. Rek, J. C. Bilello and S. M. Yalisove, *Surface Roughness and In-Plane Texturing in Sputtered Thin Films*, J. Appl. Phys. 84, (1998), 1346-1353.

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## Reports

John C. Bilello, "Advanced Tribological Coatings", Renewal Report to Stanford Synchrotron Radiation Laboratory, (2002), SSRL no. 2592.

M.J. Daniels, Z.U. Rek, and J.C. Bilello, *Phase Determination for Enhancement of Tribological Properties in the* Al-Cu-Fe-Cr *Quasicrystalline System,* Stanford Synchrotron Radiation Laboratory Activity Report, (2000), Proposal 2592.

J. Mirecki Millunchick, S. Manville, C. Dorin, Z. U. Rek, and J. C. Bilello, A Study of III-V Compound Semi-conductor Thin Films Using Synchrotron Topography, Stanford Synchrotron Radiation Laboratory Activity Report, (2000), Proposal 2652.

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J. Hershberger, Z. U. Rek, S. M. Yalisove, and J. C. Bilello, *Strain in Mo Buried Layers,* Stanford Synchrotron Radiation Laboratory Activity Report, (1998), Proposal 2346MP.

Z. B. Zhao, S. M. Yalisove, Z. U. Rek and J. C. Bilello, *Analysis of Phases and Texture in Reactively Sputtered $Cr_xN_y$ Thin Films,* Stanford Synchrotron Radiation Laboratory Activity Report, (1998), Proposal 2346MP.

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Z. B. Zhao, Z. U. Rek, and J. C. Bilello, *Real Time Observation of Film Cracking and Delamination via High Temperature X-ray Topography*, Stanford Synchrotron Radiation Laboratory Activity Report, (1997), Proposal 2346MP.

Z. B. Zhao, J. Hershberger, A. Chiaramonti, Z. U. Rek and J. C. Bilello, *Synchrotron X-Ray Topographic Studies on Deformation of Single Crystals*, Stanford Synchrotron Radiation Laboratory Activity Report, (1997), Proposal 2346MP

Theses:

Jay F. Whitacre, Doctoral Thesis, 2000
*Impurity incorporation, deposition kinetics, and microstructural evolution in sputtered Ta films*, Now Senior Scientist JPL, Pasadena, CA

Zhibo B. Zhao, Doctoral Thesis, 1999

*Evolution of microstructure and residual stress in sputtered Cr and CrxNy thin films*, Now Staff Scientist at Delphi Automotive Group, Shelby Twsp, Michigan.

Jeff G. Hershberger, Doctoral Thesis, 1999
*Strain and structure of amorphous boron carbide and silicon carbide thin films*, Now Research Scientist Tribology Group, Argonne National Laboratories, Argonne, Illinois.

Beth Ann Rainey, Master of Science, August 2000, Now working at IBM in Burlington, Vermont.

Ankur Agurwal, Master of Science, August, 2000. Now working at AMD, in Sunnyvale, California.

## Symposium and other Conference Presentations:

M.J. Daniels, D. King, J.S. Zabinski, Z.U. Rek[4], and J.C. Bilello, *Microstructure and Chemistry of Annealed AlCuFeCr Quasicrystalline Coatings*, AVS Symp. F - Inter. Conf. On Metall. Coatings and Thin Films - 2002, San Diego, CA, April 2002.

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J. C. Bilello, *High-Resolution Synchrotron X-ray Scattering of the Nanostructure of Surface Composite Coatings*, Invited talk at TMS Symposium on 'Surface Composite Coatings', TMS Fall Meeting, October, 2001, Indianapolis, IN.

A.B. Agarwal, B. A. Rainey, S. M. Yalisove, J. C. Bilello, *Nanoindentation and Microstructural Evolution Studies of DC Magnetron Sputtered Chromium Nitride Thin Films*, Spring meeting of the Materials Research Society, April, 2001, San Francisco, CA.

M. J. Daniels, J.C. Bilello, D. Hyland, D. Dew-Hughes, C.R.M. Grovenor, *High Resolution X-ray Characterization of Tl-2212 Superconducting Thin Films*, Spring meeting of the Materials Research Society, April 2001, San Francisco, CA.

S.M. Yalisove and J.C. Bilello, *In-Situ x-ray diffraction during sputter deposition of thin films*, Spring meeting of the Materials Research Society, April 2000. San Francisco, CA,.

J.C. Bilello and S.M. Yalisove, *Impurity effects in the initial stages of refractory metal sputter deposition studied via real-time in situ x-ray methods,* Spring meeting of the Materials Research Society, April 2000, San Francisco, CA.

J. F. Whitacre, Z. U. Rek, S M. Yalisove, and J. C. Bilello, *Relating Phase Content to Deposition Kinetics in Ultra-Thin Sputtered Tantalum Films,* Fall 1999 meeting of Amer. Vac. Society.

J. F. Whitacre, Z. U. Rek, J. C. Bilello and S. M. Yalisove, *In-Plane Texture in Evaporated Cr Films,* Fall 1999 meeting of Amer. Vac. Society.

J. F. Whitacre, Z. B. Zhao, B. A. Rainey, S. M. Yalisove, and J. C. Bilello, *Metallic Sputtered Film Evolution Via Real-time/In-situ X-ray Diffraction,* Fall 1999 meeting of Amer. Vac. Society

J. F. Whitacre, Z. U. Rek, J. C. Bilello, and S M. Yalisove, *Testing a Model Used to Describe In-Plane Texturing In Sputtered Mo Films.* Materials Research Society, December 1997 Meeting, Boston MA, Symposium A: Evolution of Surface Morphology and Thin-Film Micro-structure.

J. F. Whitacre, S. M. Yalisove, and J. C. Bilello, Real-Time *In-Situ X-Ray Diffraction Studies of Sputter Deposited Thin Films,* Materials Research Society, December 1997 Meeting, Boston MA, Symposium A: Evolution of Surface Morphology and Thin-Film Microstructure.

Talks at Department of Defense facilities:

John C. Bilello, M. J. Daniels and C. R. M. Grovenor, *Characterization of As-Sputtered and Annealed Quasicrystals* February 1, 2002, DARPA, Institute for Defense Analysis, Arlington, VA.

## Personnel:

### Faculty and other senior collaborators:

John C. Bilello, Professor, University of Michigan, Principal Investigator

Zofia U. Rek, Senior Research Scientist, Stanford Synchrotron Radiation Laboratory, Menlo Park, CA.

Chris Grovenor, Reader and Deputy Head, Department of Materials, Oxford University, Oxford, United Kingdom.

### Post-Doctoral Associates:

None

### Graduate Research Assistants:

Benjamin French (started January 2000) passed written Ph. D. qualifying exam February 2000, passed Oral Ph. D. exam December 2001. Needs only to finish Thesis - expected completion date August 2004.

Matthew J. Daniels (started July 1, 1999) passed written Ph. D. qualifying exam September 2000, Passed oral Ph.D. exam March 2001. Needs only to finish Thesis – expected completion date August 2003.

Michelle Tokarz, (started September 2000) passed written Ph. D. qualifying exam February 2001 Passed oral Ph.D. exam November 2002,

### Students who worked on this grant and have graduated:

Zhibo Zhao (Ph. D. awarded August 1999) – Staff member, Delphi Automotive Research Laboratory, Shelby Twsp, MI.

Jeff Herschberger (Ph. D. awarded August 1999) - Staff Scientist, Argonne National Laboratory, Argonne, IL.

Jay F. Whitacre (Ph. D. awarded August 2000) - Staff Scientist Jet Propulsion Laboratory, Pasadena, CA.

Beth Ann Rainey (M.S. awarded December 2000) - now at IBM, Burlington, VT.

Ankur Bhushan Agarwal (M. S. awarded December 2000) - now at AMD, Sunnyvale, CA.